4 Analysis of Variations in Toxic Air Contaminants

4.1 Day-of-Week Patterns for Six High-Risk Toxic Air Contaminants

4.1.1 Abstract

Day-of-week means were computed for six high-risk toxic air contaminants (TACs): 1,3-butadiene, benzene, acetaldehyde, formaldehyde, carbon tetrachloride, and perchloroethylene. Statistical tests were performed to assess the statistical significance of differences between days of the week. Benzene and 1,3-Butadiene, emitted mainly by mobile sources, exhibit lower concentrations on weekends compared to weekdays. Perchloroethylene, used primarily as a dry-cleaning solvent, is also lower on weekends compared to weekdays. Formaldehyde, acetaldehyde, and carbon tetrachloride do not show a day-of-week pattern. Because TACs are collected as 24-hour samples, they do not shed much light on day-of-week variations in ozone concentration. However, they are of intrinsic interest because of their human health implications.

4.1.2 Background

Routine sampling for Toxic Air Contaminants began in California in 1985. Today, roughly 70 compounds are measured at approximately 30 sites. These compounds come from a wide variety of sources, including motor vehicles, industrial plants, and waste disposal sites, among others.

In recent years, rapid progress has occurred for some TACs. For example, between 1990 and 1997, annual average concentrations of benzene and 1,3-butadiene decreased substantially in the South Coast Air Basin. Aggregate data from five monitoring sites indicate that concentrations of benzene and 1,3-butadiene decreased by more than 70% and 40% respectively.

Emission patterns vary from one compound to another. Some compounds, such as those emitted by mobile sources, can be expected to show a distinct day-of-week emission cycle. Because TACs are collected as 24-hour canister samples, they do not have sufficient resolution to shed much light on day-of-week differences in ozone formation. However, because TACs have significant human health implications, they are themselves of intrinsic interest. This study represents an attempt to confirm whether statistically significant day-of-week patterns can be observed for several of the more prevalent TACs.

We analyzed ambient concentrations of six of the highest-ranked TACs in terms of total estimated excess lifetime cancer cases in California. This study focused on data collected in the Los Angeles area between 1989 and 1998. During that period, six ARB TAC sites were operational in the Los Angeles area – Burbank, Los Angeles, North Long Beach, Rubidoux, Simi Valley, and Upland. Data are not available for all sites and compounds throughout the study period. All data were taken from the ARB's official TAC database (ARB Air Quality Data web site).

Additional high-risk TACs that were not analyzed include diesel particulate matter, para-dichlorobenzene, and hexavalent chromium. Diesel particulate matter was not considered because ambient data are not available. Para-dichlorobenzene and hexavalent chromium were dropped from the analysis because most of the ambient measurements were below the limit of detection (LOD).

4.1.3 Methodology

Data analysis fell broadly into four steps:

4.1.3.1 Data quality screening

Two obvious outliers, out of 7,001 observations, were dropped from the analysis. Where data were reported as below LOD, b s of the LOD was substituted, based on a linear approximation to the left tail of the data distribution. Investigations suggested that for a variety of assumed data distributions, this is a better choice than the conventional 2 LOD.

4.1.3.2 Adjustment for trend and seasonality

Data were adjusted for seasonality and trend by taking residuals (differences between actual and fitted values) from a smoothing spline. Splines have an advantage over other smoothing methods when applied to complex datasets in that their degree of smoothness is locally adaptive, rather than being uniform over the range of the data (Simonoff, 1996). The degree of smoothness was initially selected by generalized cross validation, then fine-tuned by eye, compound by compound, to yield a curve which followed the seasonal pattern and trend without excessive roughness (Figure 4.1-1, upper half). The residuals from the spline fit, henceforth referred to as the seasonally adjusted data, were largely uncorrelated and symmetrically distributed (Figure 4.1-1, lower half).

4.1.3.3 Computation of group means

Group means and standard errors were computed treating the seasonally adjusted data for different days of week as independent. The assumption of independence is reasonable because TAC samples are collected 12 days apart, long compared to the time scale of meteorological events which impact atmospheric concentrations.

4.1.3.4 Statistical comparison

Days of the week were compared by examining error bar charts of mean seasonally adjusted concentrations by day-of-week (Figure 4.1-2). The width of the error bars was set to a 97.5% confidence interval to yield a conservative 95% confidence level for pairwise comparisons between days.

To ensure that the seasonal adjustment procedure did not introduce artifacts, "raw" means were computed without seasonal adjustment. While there were minor differences between the means of the raw and seasonally adjusted data, it made no difference to the overall conclusions.

To confirm the statistical results, the SAS GLM (general linear model) procedure was used to perform analysis of variance on day-of-week means, including fixed effects for month crossed with year. In order to stabilize the error variance and reduce the effect of extreme observations, the data were transformed according to the relationship $y = \log(x + \mathit{offset})$, where *offset* varied from compound to compound. GLM significance levels for pairwise comparisons of days of week were compared against the error bar charts. The results were essentially identical. GLM tends to report slightly higher significance levels than the charts, which is expected since the confidence bounds used to generate the charts are conservative.

4.1.4 Results

The analysis yielded the following results for the six compounds studied:

1,3-butadiene	Sunday is the lowest day of the week at all sites, often significantly different from mid-week. The Saturday mean concentration is comparable to weekdays, but generally slightly lower than Friday. Concentrations at many sites exhibit a slight dip on Wednesday.
benzene	Site-by-site results are virtually identical with 1,3-butadiene.
acetaldehyde	Data are only available for 1996-1998. No discernible pattern was observed.
formaldehyde	Data are only available for 1996-1998. No discernible day-of-week pattern was observed, but site-by-site results are virtually identical with acetaldehyde.
carbon tetrachloride	No discernible pattern was observed.
perchloroethylene	Sunday is strikingly lower and less variable than other days of the week. Saturday is lower than weekdays, except at Long Beach, where it is comparable to weekdays.

4.1.5 Discussion

Benzene and 1,3-butadiene are mainly emitted by mobile sources (ARB, 1996). The lower weekend concentrations probably reflect the reduced traffic volumes reported in Chapter 7.2.

Perchloroethylene is used primarily as a dry cleaning solvent (ARB, 1996). The reduced concentrations on weekends presumably reflect a weekly work cycle.

Carbon tetrachloride, once widely used as a refrigerant, propellant and industrial solvent in the United States, is currently being phased out. However, due to its long atmospheric persistence, tropospheric accumulation has created a global background concentration estimated at 1.1 – 1.5 ppb. Ambient concentrations in California probably represent global background plus a minor contribution from local sources. It is therefore not surprising that carbon tetrachloride fails to exhibit a day-of-week pattern (ARB, 1996).

The absence of day-of-week patterns for formaldehyde and acetaldehyde is something of a surprise. Ambient concentrations are believed to be dominated by photochemically generated aldehydes (ARB, 1996). Therefore, one would expect the aldehydes to show a distinct weekly pattern of some sort, just as ozone does. The absence of a discernible pattern may be due to the obscuring effect of high day-to-day variability.

4.1.6 Conclusion

Day-of-week patterns in TACs are of marginal interest for investigating the Weekend Effect in photochemical ozone formation. The TAC network was designed to monitor for the presence of toxic compounds in urban areas. Because of limitations on sampling schedule, sampling period, analytical method, and geographical coverage, TAC data are poorly suited to answering questions about photochemistry. However, day-of-week patterns in TACs are of interest for two reasons. First, it is of general interest to the scientific and public health communities to understand the temporal pattern of TAC concentrations because TACs pose a significant risk to human health. Second, the day-of-week patterns in TACs can serve to confirm or contradict findings based on other datasets such as PAMS hydrocarbon monitoring.

Regarding reason (1), the previous section discussed how the findings of this analysis, other than the lack of a significant day-of-week pattern for the aldehydes, generally support the conventional view of day-of-week patterns in TACs (ARB, 1996).

Regarding reason (2), the TAC analysis confirms the finding of lower hydrocarbon concentrations on weekends reported in Chapter 5.3 on VOC/NO_X ratios. Of the TACs analyzed, benzene and 1,3-butadiene overlap with the PAMS hydrocarbon dataset analyzed in Chapter 5.3. These TACs show a distinct pattern of lower concentrations on weekends. Since these TACs are believed to be emitted mainly by motor vehicles, this finding is also consistent with the reduced motor vehicle traffic on weekends discussed in Chapter 7.

4.1.7 Recommendations

Improved characterization of weekday-weekend differences for TACs might be achieved in two complementary ways. First, the sampling frequency could be increased from the current 1-in-12 day schedule to a 1-in-6 day or even a 1-in-3 day schedule. The present sampling rate provides approximately four measurements per year for each day of the week. A 1-in-6 day schedule would provide eight samples per day of the week and a 1-in-3 day schedule would provide seventeen samples per day of the week. With quadruple the number of samples for a 1-in-3 day schedule, the precision of the annual average for each day of the week would improve by 50%.

A second way to improving the characterization of any TAC weekend effects would be to deploy more accurate instruments with improved resolution. If newer equipment required less labor and less time in the laboratory, deploying such instruments might also allow an increase in the sampling frequency without requiring more personnel or more laboratory resources.

Additionally, more hazardous air pollutants related to NOX chemistry should also be investigated(e.g., nitro-polycyclic aromatic hydrocarbons) as the data bases grow and statistical robustness increases.

4.1.8 References

ARB Air Quality Data web site: http://www.arb.ca.gov/aqd/aqd.htm.

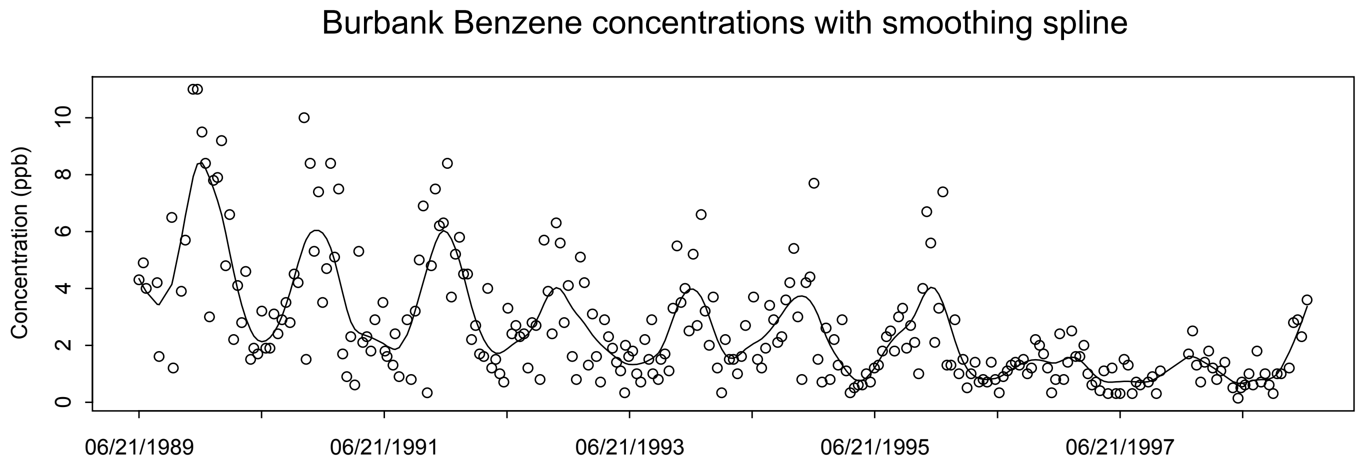
Simonoff, J. S. (1996), *Smoothing Methods in Statistics,* Springer Verlag, New York.

Air Resources Board (1996), Toxic Air Contaminant Identification List, Compound Summaries (Draft), January, 1996.

Explanation of Error Bar Charts

The attached error bar charts (Figure 4.1-2) show the means of the seasonally adjusted concentrations (residuals from the smoothing splines) by day of week, with error bars showing 97.5% confidence intervals for individual means. If the error bars for two days do not overlap, the means are significantly different at the 95% level of confidence. If two error bars do overlap, the result is inconclusive; it does not necessarily mean that the two means are the same, only that the difference between them is small relative to day-to-day variation. Note that the vertical scale is different from one compound to another. Numbers next to the means indicate sample sizes.

Figure 4.1-1. Smoothing Spline



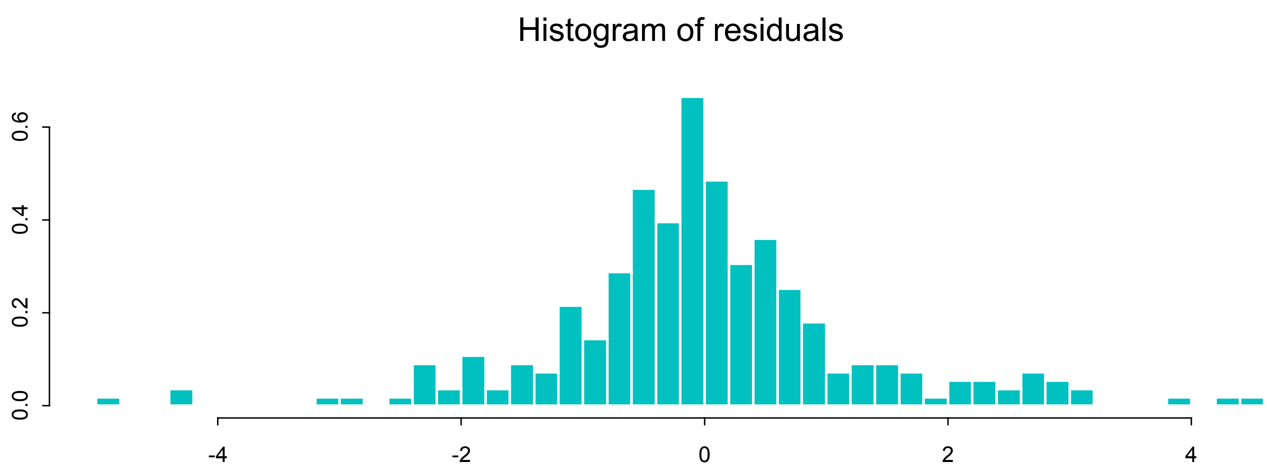
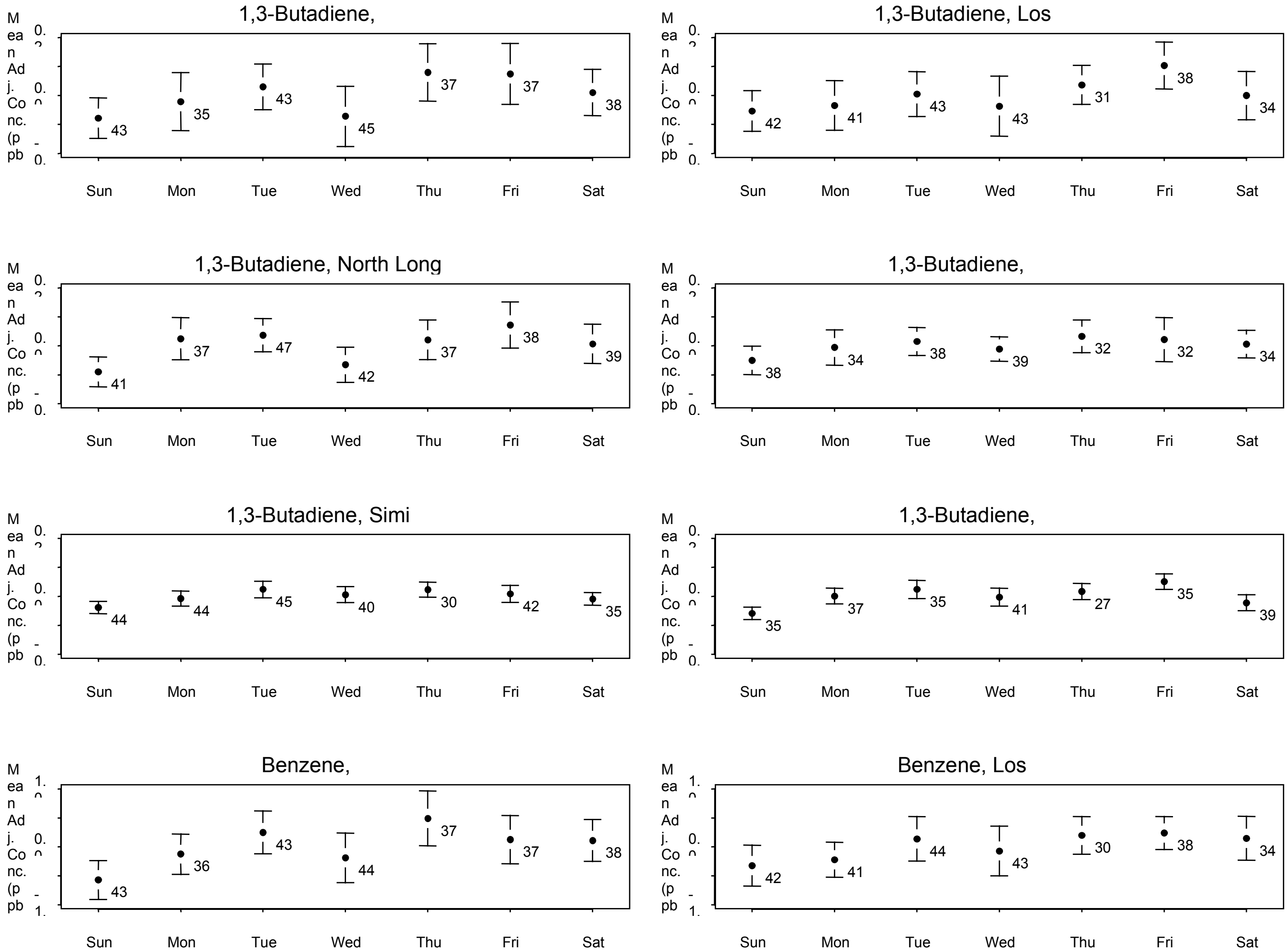
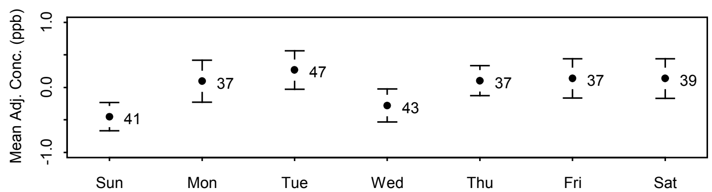


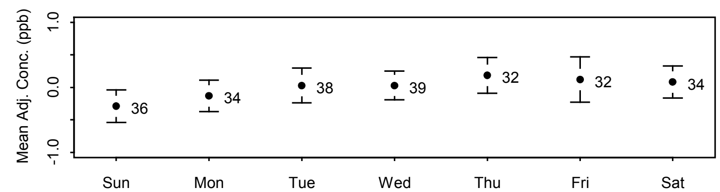
Figure 4.1-2. Day-of-week means by compound



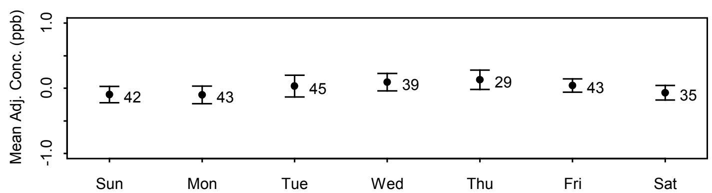
Benzene, North Long Beach



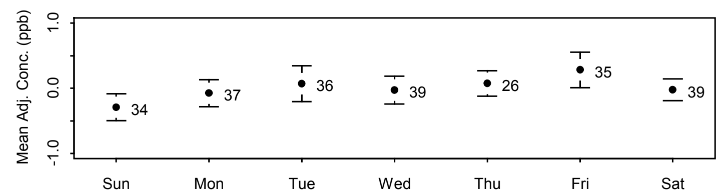
Benzene, Rubidoux



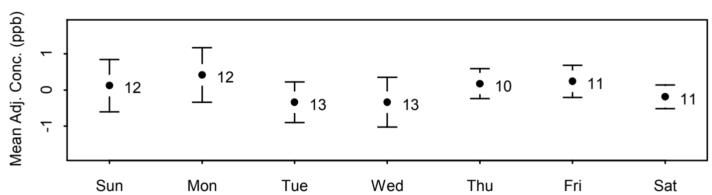
Benzene, Simi Valley



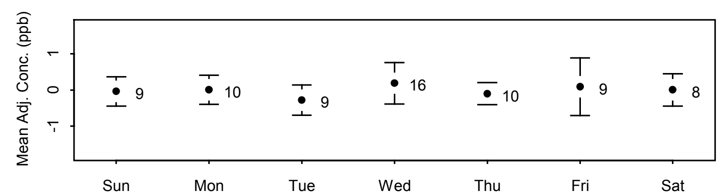
Benzene, Upland



Acetaldehyde, Burbank



Acetaldehyde, Los Angeles



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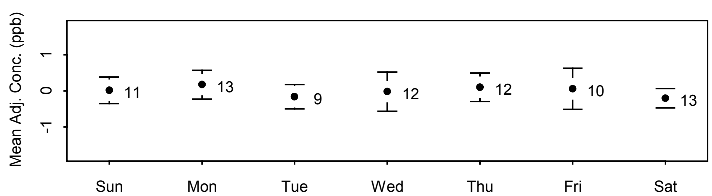
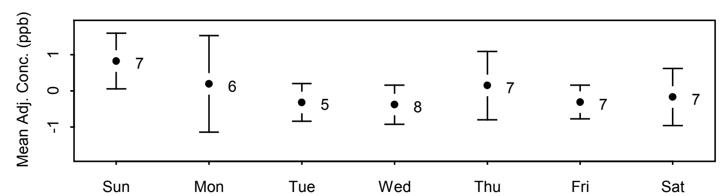
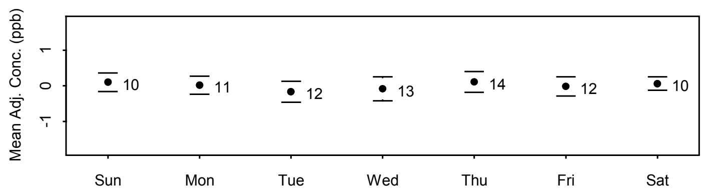


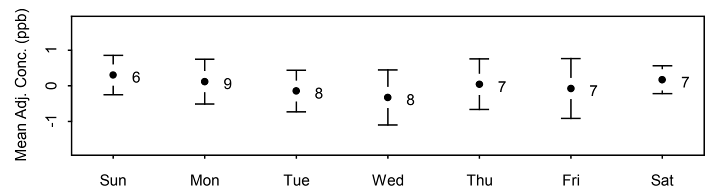
Acetaldehyde, Rubidoux



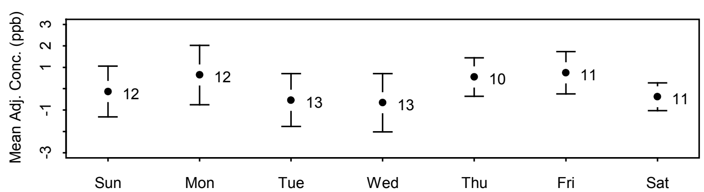
Acetaldehyde, Simi Valley



Acetaldehyde, Upland



Formaldehyde, Burbank



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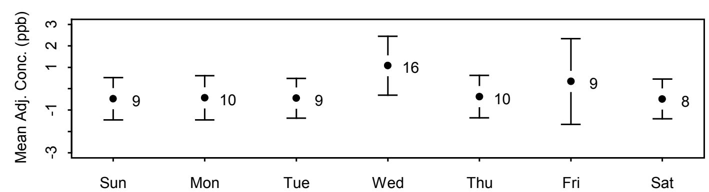
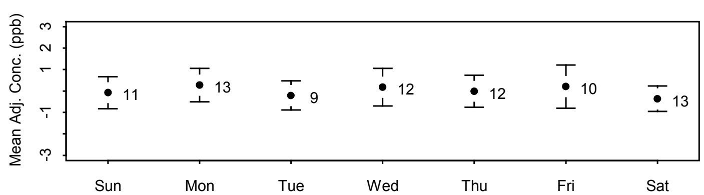
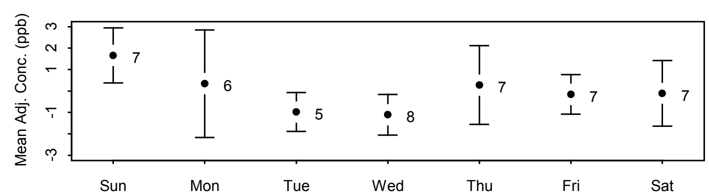


Formaldehyde, North Long Beach



Formaldehyde, Rubidoux



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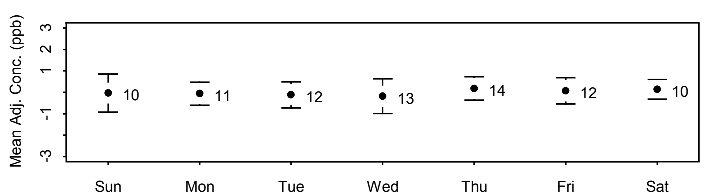
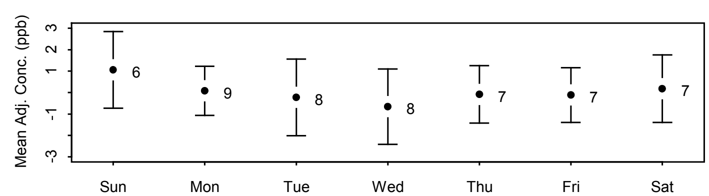
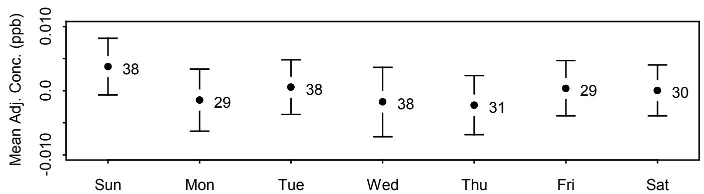


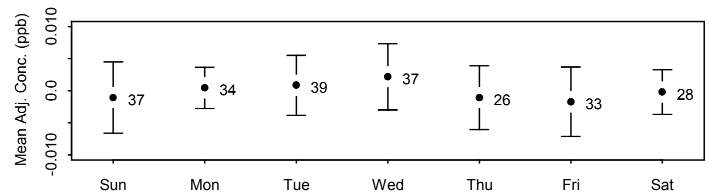
Formaldehyde, Upland



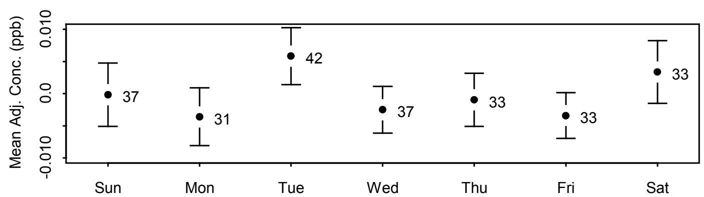
Carbon Tetrachloride, Burbank



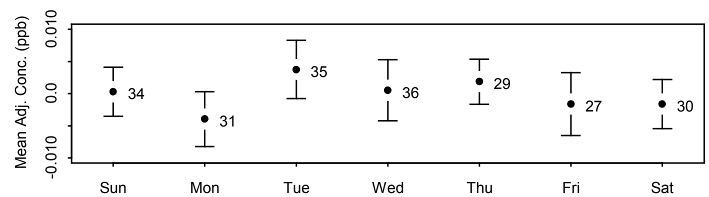
Carbon Tetrachloride, Los Angeles



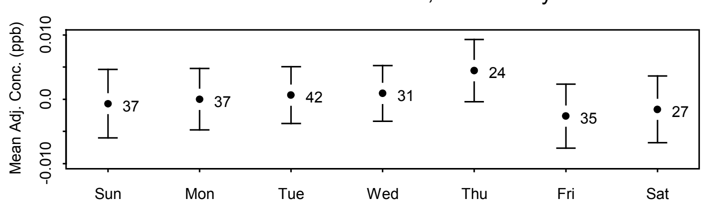
Carbon Tetrachloride, North Long Beach



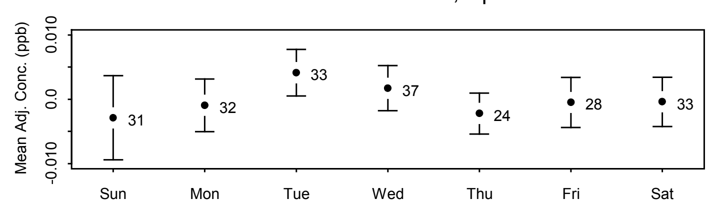
Carbon Tetrachloride, Rubidoux



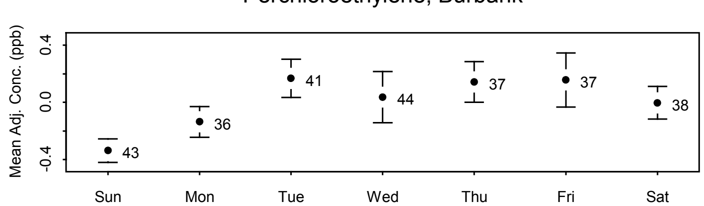
Carbon Tetrachloride, Simi Valley



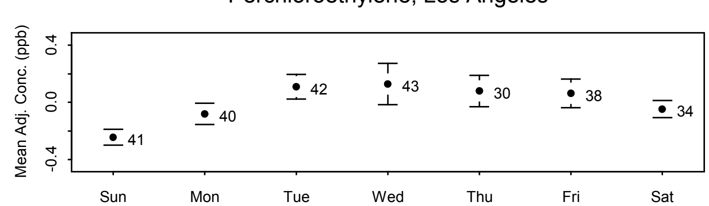
Carbon Tetrachloride, Upland

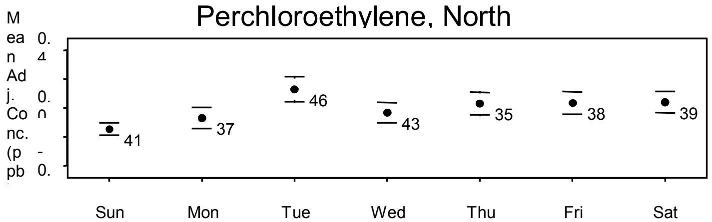


Perchloroethylene, Burbank



Perchloroethylene, Los Angeles

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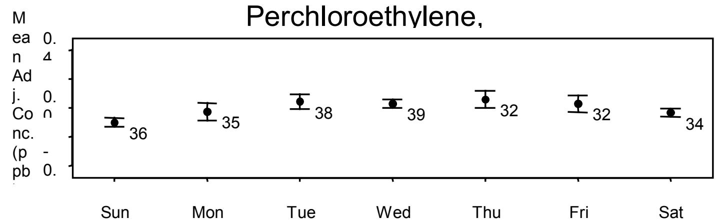
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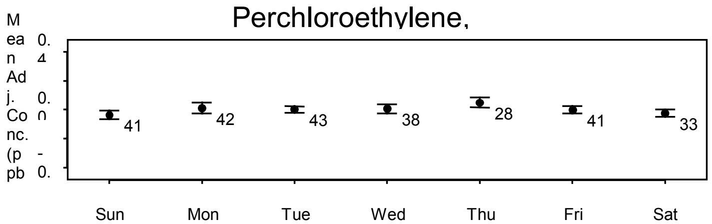
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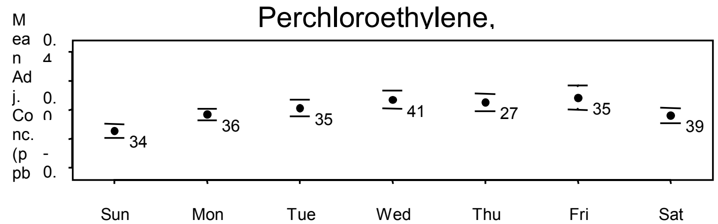
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